

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

**EP 0 156 464 B1**

(12)

## EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention  
of the grant of the patent:  
22.05.1996 Bulletin 1996/21

(51) Int Cl.<sup>6</sup>: C08F 210/02, C08F 232/08,  
C08G 61/08  
// (C08F210/02, 232:08),  
(C08F232/08, 210:02)

(21) Application number: 85300706.0

(22) Date of filing: 01.02.1985

(54) **Random copolymer**

Statistische Copolymere

Copolymères statistiques

(84) Designated Contracting States:  
DE FR GB IT NL

(30) Priority: 03.02.1984 JP 16995/84  
12.11.1984 JP 236828/84

(43) Date of publication of application:  
02.10.1985 Bulletin 1985/40

(60) Divisional application: 93202803.8

(73) Proprietor: MITSUI PETROCHEMICAL  
INDUSTRIES, LTD.  
Tokyo 100 (JP)

(72) Inventors:  
• Kajiura, Hirokazu  
Ohtake-shi Hiroshima-ken (JP)

• Oda, Hidekuni  
Iwakuni-shi Yamaguchi-ken (JP)  
• Minami, Syuji  
Ohtake-shi Hiroshima-ken (JP)

(74) Representative: Cresswell, Thomas Anthony et al  
J.A. KEMP & CO.  
14 South Square  
Gray's Inn  
London WC1R 5LX (GB)

(56) References cited:  
FR-A- 1 535 460      FR-A- 2 276 320  
US-A- 3 494 897      US-A- 4 178 424

**EP 0 156 464 B1**

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

## Description

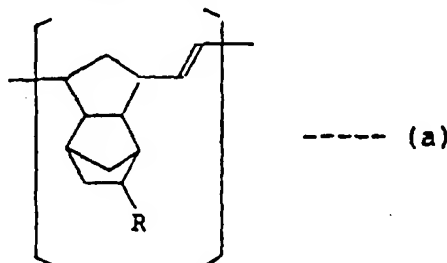
This invention relates to a random copolymer consisting essentially of a 1,4,5,8-di-methano-1,2,3,4,4a,5,8,8a-octahydronaphthalene, ethylene and an alpha-olefin of at least 3 carbon atoms and/or a cycloolefin as monomers. More specifically, it relates to a random copolymer having excellent transparency and a well balanced combination of heat resistance, heat aging resistance, chemical and solvent resistance, dielectric properties and mechanical properties such as rigidity.

Polycarbonate, poly(methyl methacrylate) and poly(ethylene terephthalate) are known as synthetic resins having excellent transparency. The polycarbonate resin has excellent heat resistance, heat aging resistance and impact strength as well as excellent transparency, but also has the defect of poor chemical resistance since it is readily attacked by strong alkalis. Poly(methyl methacrylate) has the defect that it is susceptible to attack by ethyl acetate, acetone and toluene, is swollen in ether, and has low heat resistance. Polyethylene terephthalate has excellent heat resistance and mechanical properties but has the defect of possessing weak resistance to strong acids or alkalis and is susceptible to hydrolysis.

Many polyolefins well known as general-purpose resins have excellent chemical resistance, solvent resistance and mechanical properties, but have poor heat resistance. Furthermore, they have poor transparency because they are crystalline. The transparency of polyolefins is generally improved by adding a nucleating agent to render the crystal structure fine, or by performing quenching to stop the growth of crystals, but such measures have not proved to be entirely effective. Rather, the addition of a third component such as the nucleating agent is likely to impair the inherent excellent properties of the polyolefins. Furthermore, the quenching method requires large scale equipment, and is also likely to reduce heat resistance or rigidity with a decrease in crystallinity.

On the other hand, methods have been proposed for producing polymers having superior transparency by copolymerizing ethylene with bulky comonomers. U. S. Patent 2,883,372 discloses a copolymer of ethylene with 2,3-dihydrodicyclopentadiene. This copolymer has a well balanced combination of rigidity and transparency but low heat resistance as shown by its glass transition temperature of about 100°C.

Japanese Patent Publication No. 14,910/1971 discloses a process for producing a homo- or co-polymer having polymerized units represented by the following formula (a)



wherein R is hydrogen or a lower alkyl group, which comprises polymerizing a 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene represented by the following formula (b)



wherein R is as defined above, alone or with a cyclic olefin selected from styrene, acenaphthylene, bicyclo-[2.2.1]heptene-2, alkyl-substituted products of the heptene and cyclopentene in the presence of an alcohol as a reducing agent using a halide of a noble metal such as ruthenium as a catalyst.

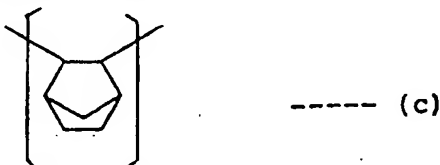
Homo- or co-polymers comprising the 1,4,5,8-di-methano-1,2,3,4,4a,5,8,8a-octahydronaphthalene as a part or the whole of monomers and methods for production thereof are also disclosed in Japanese Laid-Open Patent Publications Nos. 159,598/1975, 127,728/1983, 51,911/1984, 81,315/1984 and 81,316/1984, FR-A-1535460 and U. S. Patent 4,178,424.

The polymers disclosed in these prior art documents are ring-opened polymers having polymerized units resulting from ring-opening of monomers as in the polymerized units represented by formula (a). As can be understood from formula (a), these ring-opened polymers are structurally characterized by the fact that the main polymer chain contains an unsaturated vinyl linkage. Because of the presence of the unsaturated vinyl linkage, these polymers have poor heat aging resistance.

All of the polymers described in the above prior art documents are ring-opened polymers obtained by the ring

scission of a monomer. U. S. Patents 3,330,815 and 3,494,897 and Journal of Polymer Science: Polymer Physics Edition, volume 12, 1607-1618 (1974) describe polymers of the type obtained by the opening of the double bond of monomer without the ring scission of the bicyclohept-2-ene skeleton of the monomer.

U. S. Patent 3,330,815 discloses that a polymer comprising polymerized units of the following formula (c)

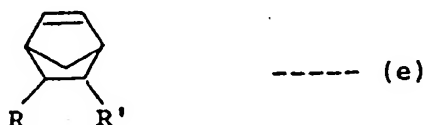


10 or the substitution product thereof is obtained from bi-cyclo[2.2.1]hept-2-ene of the following formula (d)



15 or its substitution product.

U. S. Patent 3,494,897 discloses a process for producing a copolymer of ethylene with a bicyclo[2.2.1]-hept-2-ene represented by the following formula (e)



25 Example 44 and claim 92 of this patent discloses a copolymer of ethylene with tetracyclo[6,2,1,1<sup>3,6</sup>,0<sup>2,7</sup>]-4-dodecene of the following formula (f) encompassed within the formula (e)



30 and ethylene. The Patent does not describe the content of the tetracyclododecene of the copolymer of Example 44. When it is calculated under the assumption that all of the tetracyclododecene charged was introduced into the polymer, the polymer contains polymerized units derived from about 2 mole% at most of the tetracyclododecene. U. S. Patent 3,494,897 does not at all describe specifically copolymers of ethylene with tetracyclododecenes other than the tetracyclo[6,2,1,1<sup>3,6</sup>,0<sup>2,7</sup>]-4-dodecene of formula (f).

35 Journal of Polymer Science: Polymer Physics Edition, volume 12, 1607-1618 (1974) discloses copolymers of ethylene and norbornene derivatives having dynamic mechanical properties. Table II of this document shows a copolymer of ethylene containing 1 mole% of polymerized units derived from the same compound as formula (f) (named octahydrodimethanonaphthalene in this document). Table IV thereof states that this copolymer has a beta-relaxation temperature of 15°C.

40 The copolymers described in these prior art references which contain only 2% at the most of octahydrodimethanonaphthalene have a glass transition temperature of about 15°C at the highest. They strongly exhibit a rubbery nature and have poor heat resistance and mechanical properties.

US-A-4195013 discloses the modification of ethylene- $\alpha$ -olefin-nonconjugated diene elastomeric polymers with a sterically hindering unhalogenated mono-olefin monomer. The modified polymers are used as tyre treads.

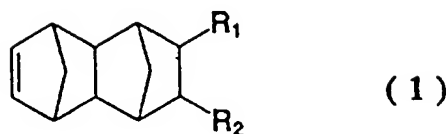
45 US-A-3494897 discloses copolymers of ethylene and bicyclo[2.2.1]hept-2-ene which contain in the polymer chain units of formula:



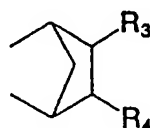
50 The invention seeks to provide copolymers having excellent transparency and a well balanced combination of heat resistance, heat aging resistance, chemical and solvent resistance, dielectric properties and mechanical properties such as rigidity.

The invention accordingly provides a random copolymer, characterised in that

55 (A) it consists essentially of (i) polymerized units derived from at least one 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene represented by the formula (1)



wherein R<sub>1</sub> and R<sub>2</sub> are the same or different and each represents a hydrogen atom, a halogen atom or an alkyl group, or R<sub>1</sub> and R<sub>2</sub> may be bonded to each other to form a trimethylene group or a group represented by the formula

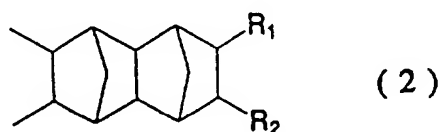


in which R<sub>3</sub> and R<sub>4</sub> are the same or different and each represents a hydrogen atom, a halogen atom or an alkyl group (ii) polymerized units derived from ethylene and (iii) polymerized units derived from at least one alpha-olefin of at least 3 carbon atoms and/or a cycloolefin in addition to that of formula (1),

(B) the mole ratio of polymerized units derived from the 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene to polymerized units derived from ethylene is from 3:97 to 95:5, preferably from 5:95 to 80:20,

(B') the mole ratio of polymerized units derived from the at least one alpha-olefin and/or cycloolefin to the polymerized units from the 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene is from 95:5 to 20:80, preferably from 90:10 to 30:70, and

(C) the 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene is incorporated in the polymer chain as polymerized units represented by formula (2)



wherein R<sub>1</sub> and R<sub>2</sub> are as defined above.

The present invention also provides a process for producing a random copolymer as defined above which comprises copolymerizing a monomer mixture consisting essentially of ethylene, at least one alpha-olefin of at least 3 carbon atoms and/or a cycloolefin, and at least one 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene of formula (1) in a hydrocarbon medium in the presence of a catalyst formed from a vanadium, titanium or zirconium compound and an organoaluminium compound which are soluble in the hydrocarbon medium and under a pressure of up to 4.9 MPa (0 to 50 kg/cm<sup>2</sup>).

The present invention further provides shaped articles of a random copolymer as defined above.

The 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene, i.e. a tetracyclo[6,2,1,1<sup>3,6</sup>,0<sup>2,7</sup>]-4-dodecene, used in this invention is represented by the above formula (1).

Examples of the halogen atom for R<sub>1</sub> to R<sub>4</sub> are fluorine, chlorine and bromine. The alkyl group for R<sub>1</sub> to R<sub>4</sub> may be linear or branched, and preferably has 1 to 20 carbon atoms, particularly 1 to 10 carbon atoms. Examples of the alkyl group include methyl, ethyl, n-propyl, isopropyl, n-butyl, iso-butyl, sec-butyl, t-butyl, pentyl, hexyl, heptyl, octyl, nonyl and decyl.

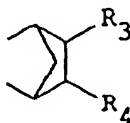
Examples of the 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene of formula (1) include

- 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,
- 2-methyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,
- 2-ethyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,
- 2-propyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,
- 2-hexyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,
- 2-stearyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,
- 2-decyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,
- 2,3-dimethyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,
- 2,3-dimethyl-3-ethyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,
- 2-methyl-3-ethyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,

2-chloro-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,  
 2-bromo-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,  
 2-fluoro-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,  
 2-cyclohexyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,  
 2-isobutyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,  
 2,3-dichloro-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,  
 12-ethyl-hexacyclo[6,6,1,1<sup>3,6</sup>,1<sup>10,13</sup>,0<sup>2,7</sup>,0<sup>9,14</sup>]-heptadecene-4,  
 12-methyl-hexacyclo[6,6,1,1<sup>3,6</sup>,1<sup>10,13</sup>,0<sup>2,7</sup>,0<sup>9,14</sup>]-heptadecene-4,  
 12-isobutyl-hexacyclo[6,6,1,1<sup>3,6</sup>,1<sup>10,13</sup>,0<sup>2,7</sup>,0<sup>9,14</sup>]-heptadecene-4,  
 hexacyclo[6,6,1,1<sup>3,6</sup>,1<sup>10,13</sup>,0<sup>2,7</sup>,0<sup>9,14</sup>]-heptadecene-4, and  
 pentacyclo[6,5,1,1<sup>3,6</sup>,0<sup>2,7</sup>,0<sup>9,13</sup>]-pentadecene-4.

These 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalenes may be used singly or in combination.

Among the compounds of formula (1), those in which at least one of R<sub>1</sub> and R<sub>2</sub> is an alkyl group, especially having 1 to 10 carbon atoms, above all 1 to 5 carbon atoms, or in which R<sub>1</sub> and R<sub>2</sub> are bonded together to form a trimethylene group or a group of the formula



wherein R<sub>3</sub> and R<sub>4</sub> are as defined above, and preferably represent an alkyl group having 1 to 10 carbon atoms, especially 1 to 5 carbon atoms, are preferred.

The compound of formula (1) can be produced, for example, by subjecting the corresponding norbornene and cyclopentadiene to a Diels-Alder reaction.

According to the process of this invention, the monomers are copolymerized in a hydrocarbon solvent in the presence of a catalyst.

The catalyst used is one formed from a vanadium compound and an organoaluminium compound which are soluble in the hydrocarbon solvent used.

Suitable vanadium compounds include vanadium halides such as VCl<sub>4</sub>, VBr<sub>4</sub>, VCl<sub>3</sub> and VBr<sub>3</sub>; vanadium oxyhalides such as VOCl<sub>3</sub>, VOBr<sub>3</sub>, VOCl<sub>2</sub> and VOBr<sub>2</sub>; and vanadium compounds of formula VO(OR)<sub>n</sub>X<sub>3-n</sub> wherein R represents a hydrocarbon group, X represents a halogen, and n is a number such that 0 < n ≤ 3. Of these the vanadium oxyhalides and the compounds of formula VO(OR)<sub>n</sub>X<sub>3-n</sub> are preferred. In the compounds of formula VO(OR)<sub>n</sub>X<sub>3-n</sub>, R is an generally an aliphatic, alicyclic or aromatic hydrocarbon group, preferably an aliphatic hydrocarbon group with 1 to 20, preferably 1 to 5, especially preferably 1 to 3, carbon atoms. The number n is such that 0 < n ≤ 3, preferably 1 ≤ n ≤ 1.5. Specific examples of these vanadium compounds are VO(OCH<sub>3</sub>)<sub>2</sub>Cl, VO(OCH<sub>3</sub>)<sub>2</sub>Cl, VO(OCH<sub>3</sub>)<sub>3</sub>, VO(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Cl, VO(OC<sub>2</sub>H<sub>5</sub>)<sub>1.5</sub>Cl<sub>1.5</sub>, VO(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Cl, VO(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>, VO(OC<sub>2</sub>H<sub>5</sub>)<sub>1.5</sub>Br<sub>1.5</sub>, VO(OC<sub>3</sub>H<sub>7</sub>)<sub>2</sub>Cl, VO(OC<sub>3</sub>H<sub>7</sub>)<sub>1.5</sub>Cl<sub>1.5</sub>, VO(OC<sub>3</sub>H<sub>7</sub>)<sub>2</sub>Cl, VO(OC<sub>3</sub>H<sub>7</sub>)<sub>3</sub>, VO(O n-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>Cl, VO(O n-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>Cl, VO(O iso-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>Cl, VO(O sec-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>, and VO(OC<sub>5</sub>H<sub>11</sub>)<sub>1.5</sub>Cl<sub>1.5</sub>. Mixtures of these may also be used. These vanadium compounds can easily be obtained by, for example, reacting VOCl<sub>3</sub> with alcohols, or VOCl<sub>3</sub> with VO(OR)<sub>3</sub>.

Suitable organoaluminium compounds used together with the vanadium compounds are compounds of formula R'<sub>m</sub>AlX'<sub>3-m</sub> wherein R' represents a hydrocarbon group, preferably an aliphatic, aromatic or alicyclic hydrocarbon group having 1 to 20 carbon atoms, especially 1 to 10 carbon atoms, X' represents a halogen atom, especially fluorine, chlorine or bromine, and m is a number such that 0 < m ≤ 3. Halogen-containing organoaluminium compounds of the above formula in which m has an average value such that 1 ≤ m ≤ 2, particularly 1.2 ≤ m ≤ 1.8, are preferred. Specific examples of these organoaluminium compounds are trialkyl aluminiums such as triethyl aluminium, triisopropyl aluminium, triisobutyl aluminium, tri(n-propyl) aluminium and tri(n-butyl) aluminium; dialkyl aluminium monohalides such as diethyl aluminium monochloride, diethyl aluminium monobromide, diisopropyl aluminium monochloride, diisopropyl aluminium monobromide, di(n-propyl) aluminium monochloride, di(isobutyl) aluminium monochloride, di(n-butyl) aluminium monochloride, di(sec-butyl) aluminium monochloride, di(n-pentyl) aluminium monochloride and dioctyl aluminium monochloride; alkyl aluminium sesquihalides such as ethyl aluminium sesquichloride, isopropyl aluminium sesquichloride, n-propyl aluminium sesquichloride, n-butyl aluminium sesquichloride, n-pentyl aluminium sesquichloride and n-octyl aluminium sesquichloride; and alkyl aluminium dihalides such as ethyl aluminium dichloride, ethyl aluminium dibromide, isopropyl aluminium dichloride, isopropyl aluminium dibromide, n-propyl aluminium dichloride, n-propyl aluminium dibromide, n-butyl aluminium dichloride, isobutyl aluminium dichloride, sec-butyl aluminium dichloride, n-pentyl aluminium dichloride and n-octyl aluminium dichloride. Mixtures of these may also be used.

The copolymerization is carried out in a hydrocarbon solvent. Examples of the solvent include aliphatic hydrocarbons having 5 to 15 carbon atoms such as pentane, hexane, heptane, octane and kerosene; alicyclic hydrocarbons having 5 to 15 carbon atoms such as cyclopentane and cyclohexane; and aromatic hydrocarbons having 6 to 15 carbon atoms such as benzene, toluene and xylene. These solvents may be used singly or in combination.

5 The mole ratios of units derived from particular monomers in the random copolymer of the invention are measured by  $^{13}\text{C}$ -NMR analysis.

The compound of formula (1) is incorporated into the chain of the random copolymer of the invention as polymerized units of formula (2) above.

10 The random copolymers of the invention, therefore, usually have an iodine number of not more than 5, and many of them have an iodine number of not more than 1. The random copolymers of this invention preferably have an intrinsic viscosity  $[\eta]$ , measured in decalin at  $135^\circ\text{C}$ , of 0.005 to 20 dl/g, more preferably 0.01 to 15 dl/g.

The novel random copolymers of this invention are generally amorphous or of low crystallinity. Preferably, they are amorphous. Accordingly, they have good transparency. Generally, these copolymers have a crystallinity, determined by X-ray diffraction, of not more than 40%; preferably not more than 25%.

15 The copolymer of the invention has a melting point, determined by a differential scanning calorimeter (DSC), of not more than  $135^\circ\text{C}$ , preferably not more than  $128^\circ\text{C}$ , or does not show a melting point.

Random copolymers of this invention in which the mole ratio of the polymerized units from the 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene to the polymerized units from ethylene is from 10:90 to 90:10, preferably from 15:85 to 80:20 (measured by  $^{13}\text{C}$ -NMR analysis), and which have an intrinsic viscosity, measured in decalin at  $135^\circ\text{C}$ , of 0.3 to 15 dl/g, preferably 0.5 to 10 dl/g, a crystallinity, determined by X-ray diffraction, of not more than 25%, preferably not more than 10%, and a melting point, measured by a differential scanning calorimeter, of not more than  $128^\circ\text{C}$ , preferably not more than  $100^\circ\text{C}$ , and a glass transition temperature measured by a dynamic mechanical analyzer (DMA) made by Du Pont of at least  $80^\circ\text{C}$ , preferably 100 to  $220^\circ\text{C}$ , have excellent transparency, processability, heat resistance, heat aging resistance, chemical and solvent resistance, dielectric properties and mechanical properties such as rigidity. Accordingly, these copolymers can be used as a transparent resin in various fields including an optical field as optical lenses, optical disks, optical fibers and window-panes, an electrical field as water tanks for electric irons, articles used for electronic ovens, substrates for liquid crystal display, substrates for printed circuit boards, substrates for high frequency circuits, and transparent electrically conductive sheets or films, medical and chemical fields as injection syringes, pipettes and animal gauges, and in other fields as camera bodies, housings of various measuring instruments, films, sheets and helmets.

Random copolymers of this invention in which the mole ratio of the polymerized units from the 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene to the polymerized units from ethylene is from 10:90 to 90:10, preferably from 15:85 to 80:20 (measured by  $^{13}\text{C}$ -NMR analysis), and which have an intrinsic viscosity, measured in decalin at  $135^\circ\text{C}$ , of 0.005 to 0.3 dl/g, preferably 0.01 to 0.3 dl/g, especially preferably 0.05 to 0.2 dl/g, a crystallinity, determined by X-ray diffraction, of not more than 25%, preferably not more than 10%, a melting point, measured by a differential scanning calorimeter, of not more than  $128^\circ\text{C}$ , preferably not more than  $100^\circ\text{C}$ , a glass transition temperature measured by a dynamic mechanical analyzer (DMA) made by Du Pont of at least  $80^\circ\text{C}$ , preferably 100 to  $220^\circ\text{C}$ , and a viscosity at  $280^\circ\text{C}$  of 100 to  $2 \times 10^5$  centipoises, preferably 100 to  $2 \times 10^4$  centipoises are of relatively low molecular weight and have excellent transparency, heat resistance, heat aging resistance, dielectric properties and chemical and solvent resistance. Hence, they are useful as synthetic waxes in various applications. For example, these low-molecular-weight random copolymers of the invention can find extensive use as candles, impregnating agents for matchwood, paper processing agents, sizing agents, rubber antioxidants, waterproofing agents for cardboards, retarders for chemical fertilizers, heat accumulating agents, ceramic binders, electric insulations for paper condensers and electric wires and cables, neutron decelerating agents, textile processing aids, water-repelling agents for building materials, protecting agents for coatings, calendering agents, thixotropy imparting agents, hardness imparting agents for the cores of pencils and crayons, substrates for carbon ink, electrophotographic toners, lubricants for molding of synthetic resins, mold mold releasing agents, resin coloring agents, hot-melt adhesives, and lubricating greases.

Novel random copolymers of the invention in which the mole ratio of the polymerized units from the 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene to the polymerized unit from ethylene is from 3:97 to 20:80, preferably from 5:95 to 10:90 (measured by  $^{13}\text{C}$ -NMR analysis), and which have an intrinsic viscosity, measured in decalin at  $135^\circ\text{C}$ , of 0.3 to 20 dl/g, preferably 1.0 to 20 dl/g, especially preferably 2 to 15 dl/g, a crystallinity, determined by X-ray diffraction, of not more than 10%, preferably not more than 5%, a melting point, measured by a differential scanning calorimeter of not more than  $128^\circ\text{C}$ , preferably not more than  $100^\circ\text{C}$ , and a glass transition temperature by DMA of 25 to  $100^\circ\text{C}$ , preferably 30 to  $80^\circ\text{C}$ , have excellent shape memorizing property and antivibration property in addition to excellent transparency, heat resistance, chemical and solvent resistance, electrical properties, optical properties and moldability, and show leather properties. Accordingly, they are useful as shape memorizing polymers and antivibration material.

The alpha-olefins having at least 3 carbon atoms making up monomer component (iii) may be linear or branched,

and preferably contain 3 to 12 carbon atoms, especially 3 to 6 carbon atoms. Examples include propylene, isobutene, 1-butene, 3-methyl-1-butene, 1-pentene, 3-methyl-1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene, 1-decene and 1-dodecene.

It should be understood that the term "cycloolefins" broadly includes not only cycloolefins in the ordinary sense of the word, but also styrene and styrene derivatives and unsaturated polycyclic hydrocarbon compounds. Specific examples of the cycloolefins include cyclobutene, cyclopentene, cyclohexene, 3,4-dimethylcyclopentene, 3-methylcyclohexene, 2-(2-methylbutyl)-1-cyclohexene, styrene, alpha-methylstyrene, norbornene, methylnorbornene, ethylnorbornene, isobutylnorbornene, 2,3,3a,7a-tetrahydro-4,7-methano-1H-indene and 3a,5,6,7a-tetrahydro-4,7-methano-1H-indene. Of these, cycloolefins having a norbornene ring, such as norbornene, 5-methyl-2-norbornene, 5-ethyl-2-norbornene, and 5-isobutyl-2-norbornene, are preferred.

When the vanadium compound and the organoaluminium compound are used as the catalyst, the concentration of the former is adjusted to 0.01 to 50 millimoles/liter, preferably 0.01 to 10 millimoles/liter, and the concentration of the latter is adjusted such that the Al:v mole ratio is at least 2:1, preferably not more than 50:1, especially preferably 3:1 to 20:1.

In view of the properties of the final random copolymer or multicomponent random copolymer, the use of the catalyst composed of a vanadium compound and an organoaluminum compound is preferred in this invention. If desired, however, the vanadium compound in the catalyst may be replaced by a titanium or zirconium compound. The vanadium-type catalyst is most preferred for the use in this invention;

The ratio of the monomers charged varies according to the composition of the desired multi-component random copolymer, the type of the reaction medium, the polymerization temperature and pressure, and the type of the catalyst. Generally, the mole ratio of ethylene to the compound of formula (1) in the reaction medium is adjusted to 1:100 to 100:1, preferably 1:50 to 50:1. The mole ratio of the alpha-olefin having at least 3 carbon atoms or cycloolefins to the compound of formula (1) is adjusted to 100:1 to 1:100, preferably 10:1 to 1:50.

The polymerization temperature is generally from -30 to 80°C, and the polymerization pressure is maintained at 0 to 50 kg/cm<sup>2</sup>. A molecular weight controlling agent such as hydrogen may be added to control the molecular weight of the copolymer.

The superior heat resistance of the random copolymer of this invention is substantiated by its high glass transition temperature. When measured by a dynamic mechanical analyser (DMA), the glass transition temperature (T<sub>g</sub>) of the multi-component random copolymer of this invention is usually at least 2°C, mostly 30 to 220°C, especially 80 to 200°C.

The heat decomposition temperature of the random copolymer of this invention is usually 350 to 420°C, mostly 370 to 400°C. The heat decomposition temperature is the temperature at which weight loss begins when the sample is heated at a rate of 10°C/min. in a stream of nitrogen by a thermobalance (TGA made by Rigaku Denki Co., Ltd.).

The random copolymer of this invention usually has a flexural modulus of  $1 \times 10^4$  to  $3 \times 10^4$  kg/cm<sup>2</sup>, and a flexural yield strength usually of 300 to 1500 kg/cm<sup>2</sup>.

It also usually has a density, determined by the density gradient tube method in accordance with ASTM D1505, of at least about 0.86 g/cm<sup>3</sup>, for example 0.86 to 1.10 g/cm<sup>3</sup>, and mostly 0.88 to 1.08 g/cm<sup>3</sup>, and a refractive index, determined by ASTM D542, of 1.47 to 1.58, mostly 1.48 to 1.56. It is substantially amorphous, and its haze, determined by ASTM D1003, is usually not more than 20%, mostly not more than 10%.

Furthermore, the random copolymer of this invention has a dielectric constant of 1.5 to 4.0, mostly 1.7 to 2.6, and a dielectric tangent of  $5 \times 10^{-3}$  to  $5 \times 10^{-5}$ , mostly  $3 \times 10^{-4}$  to  $9 \times 10^{-5}$ , when they are measured in accordance with ASTM D150 at 1 kHz. It also has excellent chemical resistance and undergoes substantially no change when exposed to acids or alkalis.

The random copolymers of this invention are molded by known methods. For example, they can be extrusion-molded, injection-molded, blow-molded, or rotationally molded by using, for example, a vent-type extruder, a twin-screw extruder, a conical twin-screw extruder, a Cokneader, a plasticator, a mixtruder, a twin conical screw extruder, a planetary screw extruder, a gear-type extruder or a screwless extruder. In the molding process, known additives such as heat stabilizers, light stabilizers, antistatic agents, slip agents, antiblocking agents, antihaze agents, lubricants, inorganic and organic fillers, dyes and pigments may be used as required.

Phenolic or sulfur-type antioxidants may be cited as examples of such additives. The phenolic antioxidants include, for example, phenols such as 2,6-di-tert-butyl-p-cresol, stearyl (3,3-dimethyl-4-hydroxybenzyl)thioglycolate, stearyl beta-(4-hydroxy-3,5-di-tert-butylphenol)propionate, distearyl 3,5-di-tert-butyl-4-hydroxybenzyl phosphate, 2,4,6-tris (3',5'-di-tert-butyl-4'-hydroxybenzylthio)-1,3,5-triazine, distearyl (4-hydroxy-3-methyl-5-tert-butylbenzyl)malonate, 2,2'-methylenebis(4-methyl-6-tert-butylphenol), 4,4'-methylenebis(2,6-di-tert-butylphenol), 2,2'-methylenebis[6-(1-methylcyclohexyl)p-cresol], bis[3,5-bis(4-hydroxy-3-tert-butylphenyl)butyric acid] glycol ester, 4,4'-butylidenebis (6-tert-butyl-m-cresol), 1,1,3-tris(2-methyl-4-hydroxy-5-tert-butylphenyl)butene, bis[2-tert-butyl-4-methyl-6-(2-hydroxy-3-tert-butyl-5-methylbenzyl)phenyl] terephthalate, 1,3,5-tris(2,6-di-methyl-3-hydroxy-4-tert-butyl)benzyl isocyanurate, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene, tetrakis[methylene-3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate]methane, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl) isocyanurate, 1,3,5-tris[(3,5-di-tert-

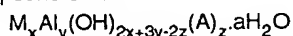
butyl-4-hydroxyphenyl)propionyloxyethyl] isocyanurate, 2-octylthio-4,6-di(4-hydroxy-3,5-di-tert-butyl)phenoxy-1,3,5-triazine and 4,4'-thiobis(6-tert-butyl-m-cresol); and polyhydric phenol/carbonic acid oligoesters such as carbonic acid oligoesters (for example, having a degree of polymerization of 2, 3, 4, 5, 6, 7, 8, 9, 10) of 4,4'-butylidenebis(2-tert-butyl-5-methylphenol).

Examples of the sulfur-type antioxidant include dialkyl thiodipropionates such as dilauryl, dimyristyl or distearyl thiodipropionate, and esters (such as pentaerythritol tetralaurylthiopropionate) formed between alkylthiopropionic acids such as butyl-, octyl-, lauryl- or stearylthiopropionic acid and polyhydric alcohols (such as glycerol, trimethylolthane, trimethylolpropane, pentaerythritol or tris-hydroxyethyl diisocyanurate).

Phosphorous-containing compounds may also be incorporated. Examples include trioctyl phosphite, triauryl phosphite, tridecyl phosphite, octyldiphenyl phosphite, tris(2,4-di-tert-butylphenyl) phosphite, triphenyl phosphite, tris(butoxyethyl) phosphite, tris(nonylphenyl) phosphite, distearyl pentaerythritol diphosphite, tetra-(tridecyl)-1,1,3-tris(2-methyl-5-tert-butyl-4-hydroxyphenyl)butane diphosphite, tetra(C<sub>12</sub>-C<sub>15</sub> mixed alkyl)-4,4'-isopropylidenediphenyl diphosphite, tetra(tridecyl)-4,4'-butylidenebis(3-methyl-6-tert-butylphenol) diphosphite, tris(3,5-di-tert-butyl-4-hydroxyphenyl) phosphite, tris(mono-di-mixed nonylphenyl) phosphite, hydrogenated 4,4'-isopropylidene diphenol polyphosphite, bis(octylphenyl).bis[4,4'-butylidenebis(3-methyl-6-tert-butylphenol)], 1,6-hexanediol diphosphite, phenyl-4,4'-isopropylidenediphenol-pentaerythritol diphosphite, bis-(2,4-di-tert-butylphenyl)pentaerythritol diphosphite, bis(2,6-di-tert-butyl-4-methylphenyl)pentaerythritol diphosphite, tris[4,4'-isopropylidenebis(2-tert-butylphenol)] phosphite, phenyldiisodecyl phosphite, di(nonylphenyl)-pentaerythritol diphosphite, tris(1,3-di-stearyloxyisopropyl) phosphite, 4,4'-isopropylidenebis(2-tert-butylphenol)-di(nonylphenyl) phosphite, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide, and tetrakis(2,4-di-tert-butylphenyl)-4,4'-biphenylene diphosphonite.

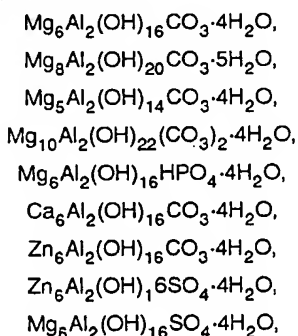
There can also be used 6-hydroxycoumarone derivatives such as alpha-, beta-, gamma- and delta-tocopherols and mixtures thereof, a 2,5-dimethyl-substitution product, 2,5,8-trimethyl-substituted product or 2,5,7,8-tetramethyl-substituted product of 2-(4-methyl-pent-3-enyl)-6-hydroxy-coumarone, 2,2,7-trimethyl-5-tert-butyl-6-hydroxycoumarone, 2,2,5-trimethyl-7-tert-butyl-6-hydroxycoumarone, 2,2,5-trimethyl-6-tert-butyl-6-hydroxycoumarone, and 2,2-dimethyl-5-tert-butyl-6-hydroxycoumarone.

It is also possible to incorporate a compound of formula

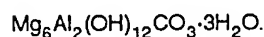


wherein M represents Mg, Ca or Zn; A is an anion other than a hydroxyl anion, x, y and z are positive numbers, and a represents 0 or a positive number.

Examples of the compounds of the above formula are



and



There may also be added an antioxidant having a 2-benzofuranone skeleton, such as 3-phenyl-2-benzofuranone and 3-phenyl-4,6-di-tert-butyl-2-benzofuranone as disclosed in Japanese Laid-Open Patent Publication No. 501,181/1980.

Examples of the light stabilizers include hydroxybenzophenones such as 2-hydroxy-4-methoxybenzophenone, 2-hydroxy-4-n-octoxybenzophenone, 2,2'-dihydroxy-4-methoxybenzophenone and 2,4-dihydroxybenzophenone; benzotriazoles such as 2-(2'-hydroxy-3'-tert-butyl-5'-methylphenyl)-5-chlorobenzotriazole, 2-(2'-hydroxy-3',5'-di-tert-butylphenyl)-5-chlorobenzotriazole, 2-(2'-hydroxy-5'-methylphenyl)benzotriazole and 2-(2'-hydroxy-3',5'-di-tert-amylphenyl)benzotriazole; benzoates such as phenyl salicylate, p-tert-butylphenyl salicylate, 2,4-di-tert-butylphenyl-3,5-di-tert-butyl-4-hydroxybenzoate and hexadecyl-3,5-di-tert-butyl-4-hydroxybenzoate; nickel compounds such as 2,2'-thiobis(4-tert-octylphenol) nickel salt, [2,2'-thiobis(4-tert-octylphenolate)]-n-butylamine nickel salt and (3,5-di-tert-butyl-4-hydroxybenzyl)phosphonic acid monoethyl ester nickel salt; substituted acrylonitriles such as methyl alpha-cyano-beta-methyl-beta-(p-methoxyphenyl)-acrylate; oxalic acid dianilides such as N'-2-ethylphenyl-N-ethoxy-5-tert-butylphenyl oxalic acid diamide and N-2-ethylphenyl-N'-2-ethoxyphenyl oxalic acid diamide; and hindered amine compounds such



as bis(2,2,6,6-tetramethyl-4-piperidine)sebacate, poly[(6-(1,1,3,3-tetramethylbutyl)-imino)-1,3,5-triazine-2,4-diyl 4-(2,2,6,6-tetramethylpiperidyl)imino]hexamethylene] and a condensation product of dimethyl succinate and 2-(4-hydroxy-2,2,6,6-tetramethyl-1-piperidyl)ethanol.

Examples of the lubricants include aliphatic hydrocarbons such as paraffin wax, polyethylene wax and polypropylene wax; higher fatty acids such as capric acid, lauric acid, myristic acid, palmitic acid, margaric acid, stearic acid, arachidic acid and behenic acid; metal salts of higher fatty acids such as lithium, calcium, sodium, magnesium and potassium salts of the above-exemplified fatty acids; aliphatic alcohols such as palmityl alcohol, cetyl alcohol and stearyl alcohol; aliphatic amides such as caproic amide, caprylic amide, capric amide, lauric amide, myristic amide, palmitic amide and stearic amide; esters formed between fatty acids and alcohols; and fluorine compounds such as fluoroalkylcarboxylic acids metal salts thereof, and metal salts of fluoroalkylsulfonic acids.

Examples of the fillers include inorganic or organic fibrous fillers such as glass fibers, silver- or aluminium-coated glass fibers, stainless steel fibers, aluminium fibers, potassium titanate fibers, carbon fibers, whiskers, Kevlar® fibers and superhigh elastic polyethylene fibers; and inorganic or organic powdery, granular or flaky fillers such as talc, calcium carbonate, magnesium hydroxide, calcium oxide, magnesium sulfate, graphite, nickel powder, silver powder, copper powder, carbon black, silver-coated glass beads, aluminum-coated glass beads, aluminium flakes, stainless steel flakes and nickel-coated graphite.

The random copolymers of this invention may be used as a blend with various known polymers. Examples of such known polymers are:

(A) Polymers derived from hydrocarbons having 1 or 2 unsaturated bonds

Polyolefins, such as polyethylene, polypropylene, polyisobutylene, poly(methylbutene-1), poly(4-methylpentene-1), poly(butene-1), polyisoprene, polybutadiene and polystyrene, or crosslinked products thereof.

Copolymers of the monomers constituting the above polymers with each other, such as ethylene/propylene co-polymer, propylene/butene-1 copolymer, propylene/isobutylene copolymer, styrene/isobutylene copolymer, styrene/butadiene copolymer, terpolymers of ethylene, propylene and dienes such as hexadiene, bicyclopentadiene and 5-ethylidene-2-norbornene, and terpolymers of ethylene, butene-1 and dienes such as hexadiene, dicyclopentadiene and 5-ethylidene-2-norborne.

Blends, grafted polymers, and block copolymers of these polymers may also be cited.

(B) Halogen-containing vinyl polymers

Polyvinyl chloride, polyvinylidene chloride, polyvinyl fluoride, polychloroprene, and chlorinated rubbers.

(C) Polymers derived from alpha,beta-unsaturated

carboxylic acids or the derivatives thereof Polyacrylate, polymethacrylate, polyacrylamide, and polyacrylonitrile.

Copolymers of the monomers constituting the above-exemplified polymers with other copolymerizable monomers, such as acrylonitrile/butadiene/styrene co-polymer, acrylonitrile/styrene copolymer, and acrylonitrile/styrene/acrylate copolymer.

(D) Polymers derived from unsaturated alcohols,

amines, acyl derivatives thereof, or acetals Polyvinyl alcohol, polyvinyl acetate, polyvinyl stearate, polyvinyl benzoate, polyvinyl maleate, polyvinyl butyral, polyallyl phthalate and polyallylmelamine.

Copolymers of the monomers constituting the above-exemplified polymers with other copolymerizable monomers, such as ethylene/vinyl acetate copolymer.

(E) Polymers derived from epoxides

Polyethylene oxide and polymer derived from hisglycidyl ether.

(F) Polyacetals

Polyoxymethylene, polyoxyethylene, and polyoxymethylene containing ethylene oxide.

(G) Polyphenylene oxide

(H) polycarbonate

(I) Polysulfone

(J) Polyurethane and urea resins

(K) Polyamides and copolyamides derived from diamines and dicarboxylic acids and/or aminocarboxylic acids or the corresponding lactams

Nylon 6, nylon 66, nylon 11, and nylon 12.

(L) Polyamide-polyethers

(M) Polyesters derived from dicarboxylic acids and dialcohols and/or hydroxycarboxylic acids or the corresponding lactones

Polyethylene terephthalate, polybutylene terephthalate and poly(1,4-dimethylolcyclohexane terephthalate).

(N) Crosslinked polymers derived from aldehydes

and phenols, urea or melamine Phenol/formaldehyde resin, urea/formaldehyde resin, and melamine/formal-

dehyde resin.

(O) Alkyd resins

Glycerin/phthalic acid resin.

(P) Unsaturated polyester resins derived from copolyesters of saturated and unsaturated dicarboxylic acids and polyhydric alcohols using vinyl compounds as crosslinking agents, and halogen-containing modified resins thereof.

(Q) Natural polymers

Cellulose, rubber and protein, or derivatives thereof, such as cellulose acetate, cellulose propionate, cellulose acetate and cellulose ether.

When the copolymers of this invention are used as synthetic waxes, they may, of course, be mixed with various known waxes.

The random copolymers of this invention may be used as a blend with each other.

The following Examples further illustrate the present invention.

#### EXAMPLE 1

A thoroughly dried 500 ml separable flask was fitted with a stirring vane, a gas blowing inlet tube, a thermometer and a dropping funnel, and thoroughly purged with nitrogen.

Toluene (250 ml), dehydrated and dried by a molecular sieve, was put into the flask.

While nitrogen was passed through the flask, 3.8 g of each of the compounds (a) in Table 1 as DMON, 3.8 g of each of the compounds (f) shown in Table 1 as cycloolefin, and 2.5 millimoles of ethyl aluminum sesquichloride were introduced into the flask, and 0.25 millimole of vanadium oxytrichloride ( $\text{VOCl}_3$ ) was added to the dropping funnel.

A gaseous mixture composed of dry ethylene (20 liters/hr) and nitrogen (40 liters/hr) was passed into the flask kept at  $10^\circ\text{C}$  for 10 minutes through the gas blowing inlet tube.

From the dropping funnel, ethyl aluminum sesquichloride was added to start the copolymerization. While passing the gaseous mixture, the copolymerization was carried out at  $10^\circ\text{C}$  for 30 minutes.

During the copolymerization, the solution was uniform and transparent, and no precipitation of the co-polymer was observed.

Methanol (5 ml) was added to the polymer solution to stop the copolymerization reaction.

The polymer solution after the stopping of the reaction was poured into large amounts of methanol and acetone to precipitate the copolymer. The precipitate was further washed with acetone, and dried in vacuo for one day at  $60^\circ\text{C}$  to obtain 8.1 g of the copolymer.

The copolymer had an ethylene content, measured by  $^{13}\text{C}$ -NMR analysis, of 55 mole%, an intrinsic viscosity, measured in decalin at  $135^\circ\text{C}$ , of 4.2 dl/g, an iodine number of 0.7, and a density, measured in accordance with ASTM D1505, of  $1.009\text{ g/cm}^3$ .

To measure its dynamical properties, the co-polymer was molded into sheets having a thickness of 1 and 2 mm by a hot press at  $230^\circ\text{C}$ . X-ray diffraction analysis of these sheets shows that no scattering by crystals was observed, and the sheets had a crystallinity ( $W^c$ ) of 0%. Transparency was measured on the 1 mm-thick sheet by a haze meter in accordance with ASTM D1003-52, and found to be 8%. The sample has a refractive index ( $n_D$ ), in accordance with ASTM D542, of 1.527. Flexural modulus and flexural yield strength were measured on the 2 mm-thick press sheet in accordance with ASTM D790, and were found to be  $2.2 \times 10^4\text{ kg/cm}^2$  and  $950\text{ kg/cm}^2$ , respectively. The glass transition temperature  $T_g$  was found to be  $135^\circ\text{C}$  by measuring the loss modulus  $E''$  at a temperature elevating rate of  $5^\circ\text{C/min}$ . by a Dynamic Mechanical Analyzer made by Du Pont, and determining  $T_g$  from its peak temperature. To determine the melting point  $T_m$ , the sample was heated at a rate of  $10^\circ\text{C/min}$ . in the range of  $-120$  to  $400^\circ\text{C}$  by DSC (990 type made by Du Pont). The melting curve (peak) was not observed. The sample also had a heat decomposition temperature, measured by a thermobalance (TGA), of  $381^\circ\text{C}$ .

The electrical properties of the copolymer were measured at 1 kHz by a dielectric loss measuring device made by Ando Electric Co., Ltd. It was found to have a dielectric constant of 2.1 and a dielectric tangent ( $\tan \delta$ ) of  $3.0 \times 10^{-4}$ .

To examine the chemical resistance of the sample, the press-formed sheet was immersed at room temperature in sulfuric acid (97%), aqueous ammonia (20%), acetone, and ethyl acetate for 20 hours, and then its appearance was observed. There was no change in colour, reduction in transparency, deformation, dissolution, nor cracking.

#### EXAMPLES 2-11

The copolymerization reaction conditions were changed as shown in Table 2, otherwise, the same operation as in Example 1 was performed. The results are shown in Tables 3-1 and 3-2. Tables 2, 3-1, and 3-2 also give the conditions and results used and obtained in Example 1.

Table 1

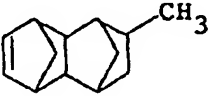
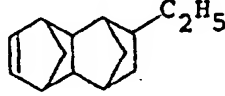
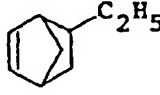
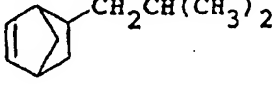
Designation	Compound
a	 <div>2-Methyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene (DMON)</div>
b	 <div>2-Ethyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene</div>
c	Propylene
d	1-Butene
e	 <div>5-Ethyl-2-norbornene</div>
f	 <div>5-iso-Butyl-2-norbornene</div>

Table 2

Example	catalyst		Amount of monomers fed				Polymerization temperature (°C)	Amount of the copolymer yielded (g)
	$\text{VOCl}_3$ (mmoles)	$\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ 1.5 (mmoles)	DMON (g)	Ethylene (g/hr)	$\alpha$ -olefin (g/hr)	Cyclo-olefin (g)		
1	0.25	2.5	(a) 3.8	20	-	(e) 3.8	10	8.1
2	"	"	(a) 5.0	"	-	(e) 2.5	"	7.9
3	"	"	(a) "	30	-	(e) "	"	9.4
4	"	"	(a) 3.8	20	-	(f) 3.8	"	7.8
5	"	"	(b) 7.5	"	(c) 30	-	"	4.9
6	"	"	(b) "	10	(c) 40	-	"	4.0
7	"	"	(a) "	20	(c) 30	-	"	4.2
8	"	"	(b) 3.8	"	(c) "	(f) 3.8	"	3.1
9	"	"	(b) "	30	(c) 20	(f) "	"	4.2
10	"	"	(b) 5.0	"	(c) "	(f) 2.5	"	4.5
11	"	"	(b) 1.0	5	(c) 5	-	"	2.8

Table 3-1

Example	$[\eta]$ (dl/g)	Monomer contents (mole%)				Iodine number	$T_g$ (°C)	$T_m$ (°C)	Heat decom- position tempera- ture (°C)	$W^C$ (%)	Density (g/cm <sup>3</sup> )	$n^D$
		DMON	Ethylene	$\alpha$ -olefin	Cyclo- olefin							
1	4.2	22	55	-	23	0.7	135	-	381	0	1.009	1.527
2	3.8	30	60	-	10	0.6	130	-	383	"	1.015	1.531
3	4.5	22	69	-	9	0.7	109	-	380	"	1.006	1.526
4	4.1	"	57	-	21	0.9	133	-	378	"	1.008	1.525
5	2.0	35	42	23	-	1.0	121	-	370	"	1.019	1.532
6	1.9	38	32	30	-	0.8	125	-	372	"	1.020	1.534
7	2.0	34	49	17	-	0.9	122	-	371	"	1.015	1.532
8	1.3	17	41	22	20	0.8	110	-	373	"	1.002	1.524
9	1.7	18	49	14	19	1.0	106	-	375	"	1.004	"
10	1.6	23	"	16	12	0.9	112	-	375	"	1.010	1.527
11	1.8	57	27	"	-	1.0	164	-	371	"	1.027	1.540

Table 3-2

Example	Haze (%)	Dielectric constant	Dielectric tangent ( $\times 10^4$ )	Flexural modulus ( $\text{kg/cm}^2$ )	Flexural yield strength ( $\text{kg/cm}^2$ )	Chemical resistance			
						97% sulfuric acid	20% aqueous ammonia	Acetone	Ethyl acetate
1	8	2.1	3.0	22000	950	○	○	○	○
2	9	2.2	4.5	20000	1030	"	"	"	"
3	10	2.1	3.6	17000	1010	"	"	"	"
4	8	2.1	4.0	21000	980	"	"	"	"
5	"	2.3	4.4	16000	600	"	"	"	"
6	9	2.4	4.5	18000	650	"	"	"	"
7	"	2.3	4.1	16000	780	"	"	"	"
8	8	2.4	4.2	19000	680	"	"	"	"
9	7	2.3	3.8	18000	700	"	"	"	"
10	9	2.4	3.9	"	720	"	"	"	"
11	10	2.4	4.6	28000	950	"	"	"	"

## EXAMPLE 12

The same copolymerization as in example 1 was carried out except that 60 g of 2-methyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene, 100 millimoles of ethyl aluminum sesquichloride and 10 millimoles of dichloroethoxyoxovanadium were used, the flow rate of ethylene was changed to 320 liters/hr, hydrogen was used instead

of nitrogen at a flow rate of 280 liters/hr, and the polymerization temperature was changed to 30°C.

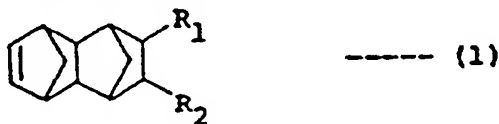
There was obtained 17.2 g of a copolymer having an ethylene content of 60 mole%, an ethylnorbornene content of 20 mole%, an intrinsic viscosity, measured in decalin at 135°C, of 0.15 dl/g, and an iodine number of 0.9. The viscosity of the copolymer, measured at 750 rpm and 280°C by an Emila-rheometer (imported by Yagami Co., Ltd.), was  $2.2 \times 10^3$  centipoises.

The copolymer was molded into a press sheet having a thickness of 1 mm at 200°C. The sheet was considerably brittle. It had a crystallinity ( $W\%$ ), determined by X-ray diffraction, of 0%. When it was subjected to a differential scanning calorimeter (Type 990 made by Du Pont) at a temperature elevating rate of 5°C/min., no melting peak was observed. The softening temperature of the copolymer, measured by a needle penetration degree measuring device of Du Pont (TMA: thermomechanical analyzer, load 49 g, quartz needle with a diameter of 0.025 mm) at a temperature elevating rate of 10°C/min., was 126°C. The copolymer had a haze, determined substantially in accordance with ASTM D1003-52, of 11%. To examine its chemical resistance, the sample was immersed for 20 hours in 97% sulfuric acid, 20% aqueous ammonia, acetone and methyl acetate, and its appearance was then observed. No reduction in colour and transparency was observed.

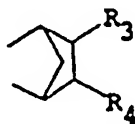
### Claims

1. A transparent random copolymer, characterised in that

(A) it consists essentially of (i) polymerized units derived from at least one 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene represented by the formula (1)



wherein  $R_1$  and  $R_2$  are the same or different and each represents a hydrogen atom, a halogen atom or an alkyl group, or  $R_1$  and  $R_2$  may be bonded to each other to form a trimethylene group or a group represented by the formula

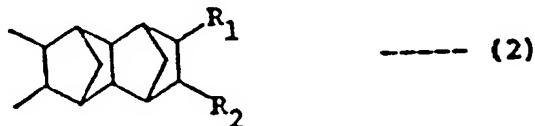


in which  $R_3$  and  $R_4$  are the same or different and each represents a hydrogen atom, a halogen atom or an alkyl group (ii) polymerized units derived from ethylene and (iii) polymerized units derived from at least one alpha-olefin of at least 3 carbon atoms and/or a cycloolefin in addition to that of formula (1),

(B) the mole ratio of polymerized units derived from the 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene to polymerized units derived from ethylene is from 3:97 to 95:5,

(B') the mole ratio of polymerized units derived from the at least one alpha-olefin and/or cycloolefin to the polymerized units derived from the 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene is from 95:5 to 20:80, and

(C) the 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene is incorporated in the polymer chain as polymerized units represented by formula (2)



wherein  $R_1$  and  $R_2$  are as defined above.

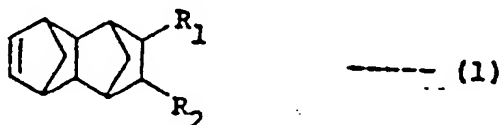
2. A random copolymer according to claim 1 which has an intrinsic viscosity, measured in decalin at 135°C, of 0.005 to 20 dl/g.
3. A random copolymer according to claim 1 or 2 wherein at least one of  $R_1$  and  $R_2$  is an alkyl group.
4. A random copolymer according to claim 1, 2 or 3 which has a glass transition temperature of at least 2°C.

5. A process for producing a random copolymer as claimed in any one of the preceding claims, which comprises copolymerizing a monomer mixture consisting essentially of ethylene, at least one  $\alpha$ -olefin of at least 3 carbon atoms and/or cycloolefin, and at least one 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene of formula (1) as defined in claim 1 in a hydrocarbon medium in the presence of a catalyst formed from a vanadium, titanium or zirconium compound and an organoaluminium compound which are soluble in the hydrocarbon medium and under a pressure of up to 4.9 MPa (0 to 50 kg/cm<sup>2</sup>).
6. Shaped articles of a random copolymer as claimed in any one of claims 1 to 4.

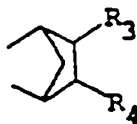
# Patentansprüche

1. Transparentes statistisches Copolymer, dadurch gekennzeichnet, daß

(A) es im wesentlichen besteht aus (i) polymerisierten Einheiten, abgeleitet von mindestens einem 1,4,5,8-Dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalin, angegeben durch die Formel (1)



wobei R<sub>1</sub> und R<sub>2</sub> gleich oder verschieden sind und jeweils ein Wasserstoffatom, ein Halogenatom oder eine Alkylgruppe bedeuten oder R<sub>1</sub> und R<sub>2</sub> miteinander verbunden sein können unter Bildung einer Trimethylen-Gruppe oder einer Gruppe, angegeben durch die Formel

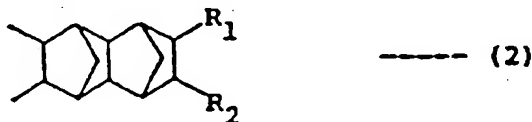


wobei R<sub>3</sub> und R<sub>4</sub> gleich oder verschieden sind und jeweils ein Wasserstoffatom, ein Halogenatom oder eine Alkylgruppe bedeuten, (ii) polymerisierten Einheiten, abgeleitet von Ethylen, und (iii) polymerisierten Einheiten, abgeleitet von mindestens einem  $\alpha$ -olefin mit mindestens 3 Kohlenstoffatomen und/oder einem Cycloolefin, zusätzlich zu demjenigen der Formel (1),

(B) das Molverhältnis von polymerisierten Einheiten, abgeleitet von dem 1,4,5,8-Dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalin, zu polymerisierten Einheiten, abgeleitet von Ethylen, 3:97 bis 95:5 beträgt,

(B') das Molverhältnis von polymerisierten Einheiten, abgeleitet von mindestens einem  $\alpha$ -Olefin und/oder Cycloolefin, zu polymerisierten Einheiten, abgeleitet von dem 1,4,5,8-Dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalin, 95:5 bis 20:80 beträgt, und

(C) das 1,4,5,8,-Dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalin in der Polymerkette eingebaut ist in Form von polymerisierten Einheiten, angegeben durch die Formel (2)



wobei R<sub>1</sub> und R<sub>2</sub> wie oben definiert sind.

2. Statistisches Copolymer nach Anspruch 1 mit einer Grundviskosität, gemessen in Decalin bei 135°C, von 0,005 bis 20 dl/g.
3. Statistisches Copolymer nach Anspruch 1 oder 2, wobei mindestens einer der Reste R<sub>1</sub> und R<sub>2</sub> eine Alkylgruppe ist.
4. Statistisches Copolymer nach Anspruch 1, 2 oder 3 mit einer Glasübergangstemperatur von mindestens 2°C.



5. Verfahren zur Herstellung eines statistischen Copolymers nach einem der vorangehenden Ansprüche, umfassend das Copolymerisieren eines Monomergemisches, bestehend im wesentlichen aus Ethylen, mindestens einem  $\alpha$ -Olefin mit mindestens 3 Kohlenstoffatomen und/oder Cycloolefin und mindestens einem 1,4,5,8-Dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalin der Formel (1), wie in Anspruch 1 definiert, in einem Kohlenwasserstoffmedium in Gegenwart eines Katalysators, gebildet aus einer Vanadium-, Titan- oder Zirkoniumverbindung und einer Organoaluminiumverbindung, die in dem Kohlenwasserstoffmedium löslich sind, und unter einem Druck von bis zu 4,9 MPa (0 bis 50 kg/cm<sup>2</sup>).

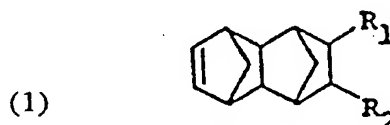
6. Formkörper aus einem statistischen Copolymer nach einem der Ansprüche 1 bis 4.

# Revendications

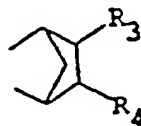
1. Copolymère statistique transparent caractérisé en ce que

(A) il est constitué essentiellement

(i) de motifs polymérisés dérivés d'au moins un 1,4,5,8-diméthano-1,2,3,4,4a,5,8,8a-octahydrogénéonaphtalène représenté par la formule (1)



dans laquelle  $R_1$  et  $R_2$  sont identiques ou différents et représentent chacun un atome d'hydrogène, un atome d'halogène ou un groupe alkyle ou  $R_1$  et  $R_2$  peuvent être liés l'un à l'autre pour former un groupe triméthylène ou un groupe représenté par la formule



dans laquelle  $R_3$  et  $R_4$  sont identiques ou différents et représentent chacun un atome d'hydrogène, un atome d'halogène ou un groupe alkyle,

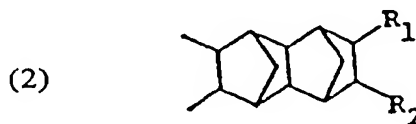
(ii) de motifs polymérisés dérivés de l'éthylène et

(iii) de motifs polymérisés dérivés d'au moins une  $\alpha$ -oléfine comportant au moins 3 atomes de carbone et/ou d'une cyclo-oléfine en plus de celle de formule (1),

(B) le rapport molaire des motifs polymérisés dérivés du 1,4,5,8-diméthano-1,2,3,4,4a,5,8,8a-octahydrogénéonaphtalène aux motifs polymérisés dérivés de l'éthylène est compris entre 3/97 et 95/5,

(B') le rapport molaire des motifs polymérisés dérivés d'au moins une  $\alpha$ -oléfine et/ou d'une cyclo-oléfine aux motifs polymérisés dérivés du 1,4,5,8-diméthano-1,2,3,4,4a,5,8,8a-octahydrogénéonaphtalène est compris entre 95/5 et 20/80,

(C) le 1,4,5,8-diméthano-1,2,3,4,4a,5,8,8a-octahydrogénéonaphtalène est incorporé dans la chaîne de polymère sous forme de motifs polymérisés représentés par la formule (2)



dans laquelle  $R_1$  et  $R_2$  sont définis comme ci-dessus.

2. Copolymère statistique conforme à la revendication 1 qui a une viscosité intrinsèque, mesurée dans la Décane à 135 °C, comprise entre 0,005 et 20 dl/g.
3. Copolymère statistique conforme à la revendication 1 ou 2 dans lequel au moins un des groupes  $R_1$  et  $R_2$  est un groupe alkyle.
4. Copolymère statistique conforme à la revendication 1, 2 ou 3 qui a une température de transition vitreuse au moins

égale à 2 °C.

5. Procédé de préparation d'un copolymère statistique conforme à une quelconque des revendications précédentes qui comprend la copolymérisation d'un mélange de monomères constitué essentiellement d'éthylène, d'au moins une  $\alpha$ -oléfine comportant au moins 3 atomes de carbone et/ou d'une cyclooléfine, et d'au moins un 1,4,5,8-diméthano-1,2,3,4,4a,5,8,8a-octahydrogénomaphthalène de formule (1) défini dans la revendication 1 dans un milieu hydrocarboné en présence d'un catalyseur formé à partir d'un composé à base de vanadium, de titane ou de zirconium et d'un composé organoaluminique solubles dans le milieu hydrocarboné et sous une pression qui peut atteindre 4,9 MPa (0 - 50 kg/cm<sup>2</sup>).
6. Articles formés en un copolymère statistique conforme à une quelconque des revendications 1 à 4.